Chemistry of Cold-Start Emissions and Impact of Emissions Control Project ID: ace153

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Annual Merit Review

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Annual Merit Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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  - John Nunan, David Moser
- **Guidance from Advisors at Ford Motor Company:**
  - Jason Lupescu, Christine Lambert

Overview

Timeline

Project start date: FY2019

Project end date: FY2021

Budget

	FY19	FY20
Task 4*: Chemistry and Control Cold-Start Emissions	$500k	$500k

- *New ORNL task in FY2019
- Part of larger ORNL response to 2018 VTO AOP Lab Call "Controlling Emissions from High Efficiency Combustion System"

Barriers

U.S. Drive Advanced Combustion & Emissions Control Roadmap Barriers & Targets

- U.S. EPA Tier 3 Bin 30 emissions
- Reduced cold start emissions
- "..HC Traps must be designed for effective control of specific HC species that are present in gasoline engine exhaust."

Collaborations

- Umicore: *advisory role & supply HC-traps and GPFs*
- Ford Motor Company: *advisory role*
- Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS)

Milestones: task specific over 3-year project

Completed

- **FY2019, Q1:** Define the different engine platforms to be tested

Completed

- **FY2020, Q1:** Completed a statistically significant LD gasoline campaign on gaseous HC emissions and PM focused on cold-start

Completed

- **FY2020, Q3:** Complete HC speciation analysis of LD HC speciation emissions and aftertreatment impacts on PM emissions and compositions

On Track

- **FY2021, Q1:** Complete a statistically significant LD cold-start sampling campaign focused on HC emissions changes over HC-Trap

On Track

- **FY2021, Q3:** Submit a manuscript on LD cold-start emissions

SMART Milestone
On Track

- **FY2021, Q4:** Completed a statistically significant hybrid cold-start campaign on gaseous HC emissions and PM

Why study the chemistry of cold-start emissions?

Relevance | Approach | Technical | Collaboration | Future Work

Barrier

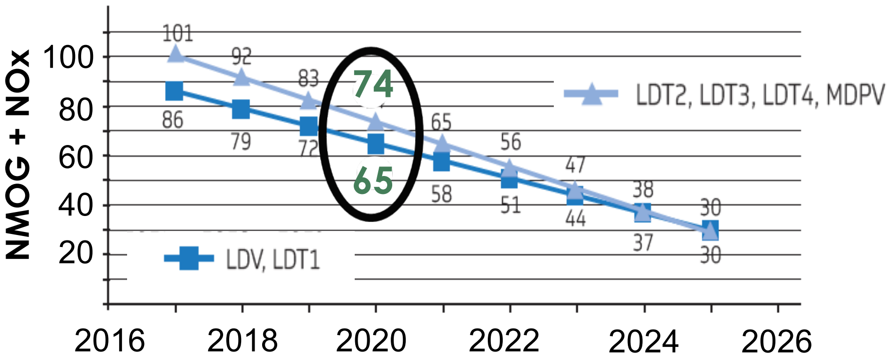
U.S. EPA Tier 3 Bin 30 emissions (NMOG + NOx)

TIER 3 FTP STANDARDS

Tier 3 Certification Bin Standards (FTP, 150,000 mi)				
Bin	NMOG+NOx (mg/mi)	PM[1] (mg/mi)	CO (g/mi)	HCHO (mg/mi)
Bin 160	160	3	4.2	4
Bin 125	125	3	2.1	4
Bin 70	70	3	1.7	4
Bin 50	50	3	1.7	4
Bin 30	**30**	**3**	**1.0**	**4**
Bin 20	20	3	1.0	4
Bin 0	0	0	0	0

Phase-in of new US Emissions Standards (2017-2025)

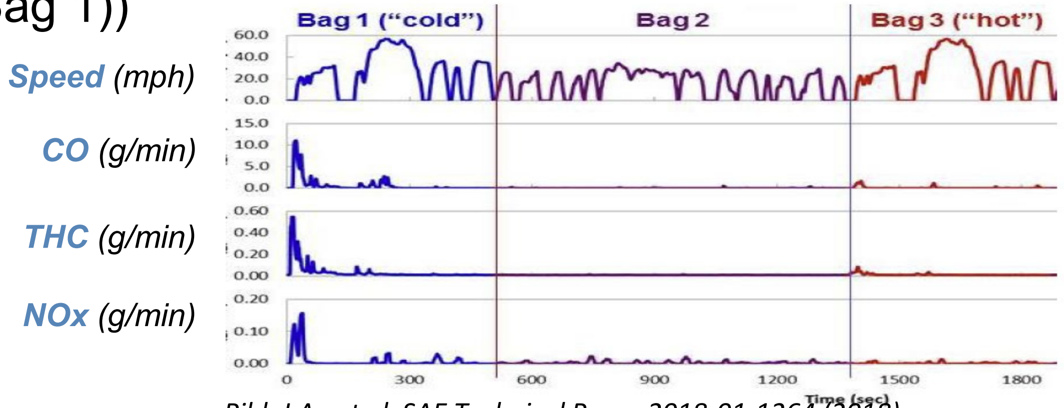
FLEET AVERAGE NMOG+NOx FTP PHASE-IN (MG/MI)



Delphi World Emissions for Passenger cars and light duty vehicles 2018-2019

Relevance

- Cold-start emissions must be addressed to meet increasingly stringent emissions regulations (90% of emissions from cold-start (Bag 1))



Pihl, J.A., et al. SAE Technical Paper 2018-01-1264 (2018).

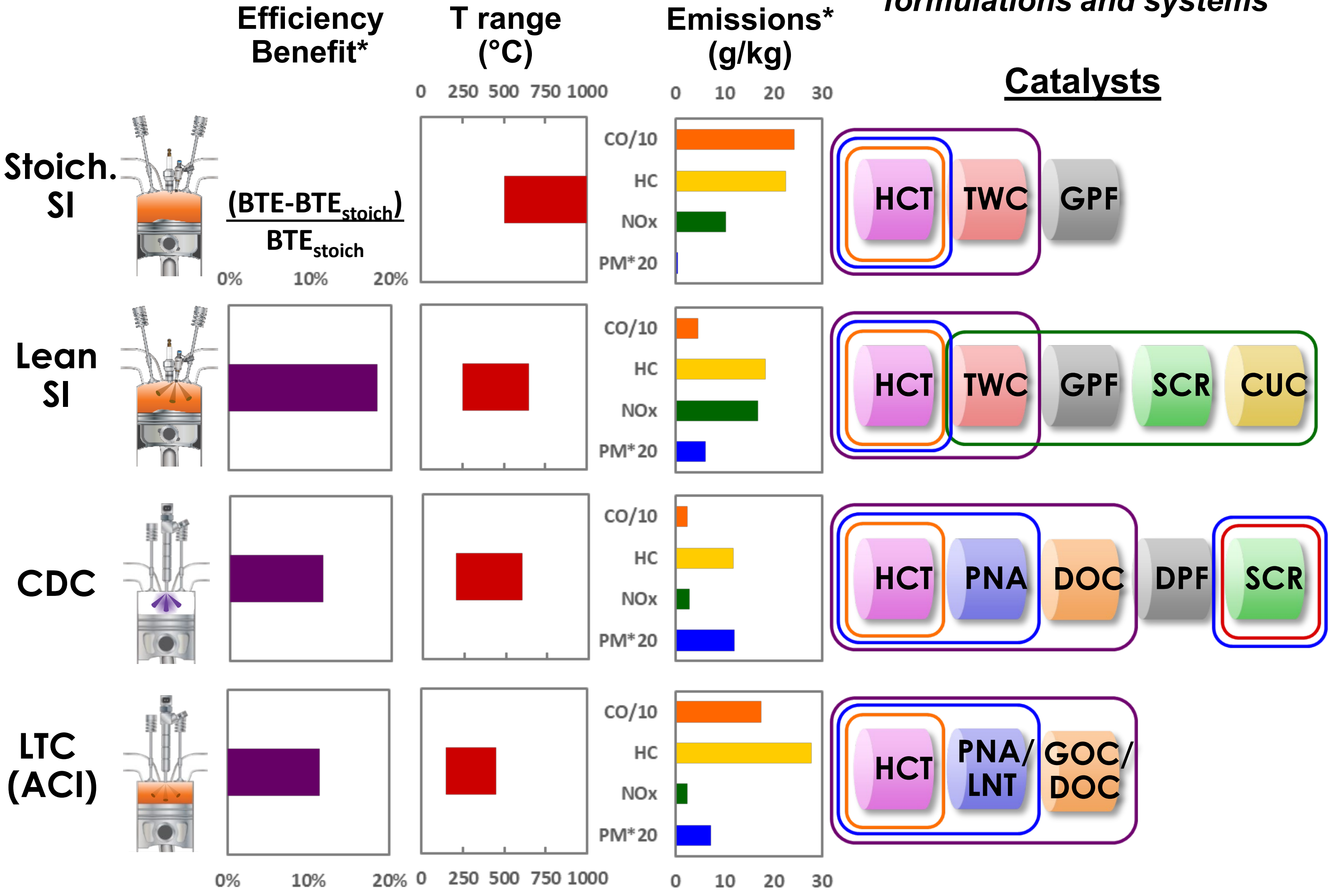
Objective/Approach

- HC-Traps are a potential emissions control solution option for reducing cold-start hydrocarbon emissions
  - All traps not uniformly effective for all HC
- Target speciation of cold-start HC emissions from consumer, on-road vehicles
  - Specifically during first 250s of FTP-75 cold-start
  - Impact of aftertreatment catalysts on speciation

NMOG (non-methane organic gases); LDV (light duty vehicle); LDT(light duty truck); MDPV (Medium duty passenger vehicles); HCT (hydrocarbon trap); HC (hydrocarbon);

Low temperature emissions control challenges affect multiple platforms

Unique emissions profiles require variety of catalyst formulations and systems



*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)

ORNL R&D portfolio spans wide range of applications, technologies, size scales, commercial readiness

ORNL Projects

CLEERS (ACE022)
Model new trap materials and aging effects on SCR catalysts

Low Temperature Emissions Control (ACE085)
Discover new low T catalysts & traps

Lean Gasoline Emissions Control (ACE033)
Develop pathways for lean gasoline engines to meet emissions with minimum fuel penalty

Chemistry & Control of Cold Start Emissions (ACE153)
Understand how exhaust chemistry impacts device performance & design

Cummins Emissions Control CRADA (ACE032)
Understand how aging affects properties and performance of SCR catalysts

See Backup Slide for abbreviations on this slide

How to study the chemistry of cold-start emissions

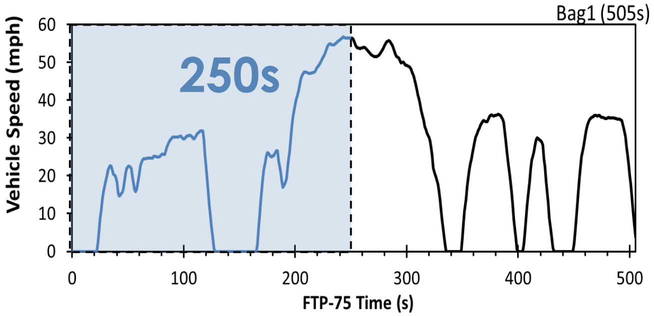
Vehicle Platforms on Chassis Dynamometer

Truck A and Truck B: MY18, GDI pick-up trucks (25-30k on-road miles)

	Engine	Exhaust Modifications
Truck A	2.7L Turbo (V6)	Removed: muffler, resonator
Truck B	5.3L NA (V8)	Removed: UB catalyst, muffler, resonator

Cold-Start:

- 1 cold-start/truck per day
  - Cold-start = 12 hour soak
- 1st, 250s of FTP-75

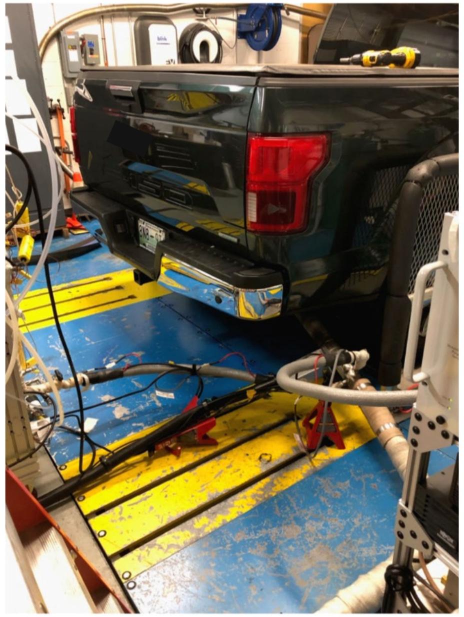


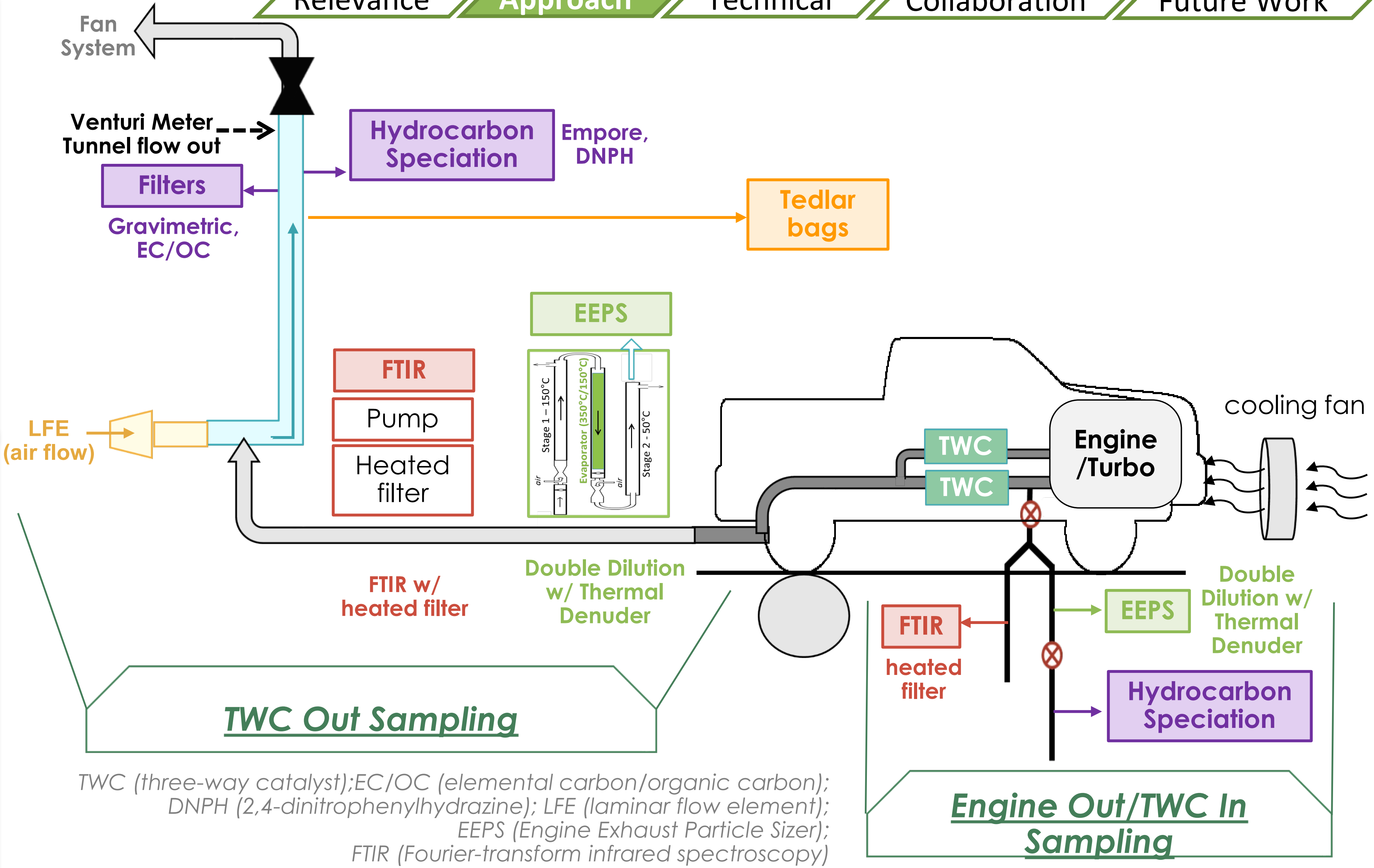
Sampling:

	Time Resolved		Cumulative 250s			
	FTIR	**EEPS**	**PM**	**Aldehydes**	**Volatile C5-C8**	**Semi-volatile C9-C18**
Engine Out	✓	✓	✓	✓	✓	✓
ccTWC Out	✓	✓	✓	✓	✓	✓
HCT out	*FY20*	*FY20*	*FY20*	*FY20*	*FY20*	*FY20*
HCT+GPF Out	*FY20*	*FY20*	*FY20*	*FY20*	*FY20*	*FY20*

UB (underbody); MY (model year); NA (naturally aspirated); cc (close coupled)

Cold-start emission Sampling Approach

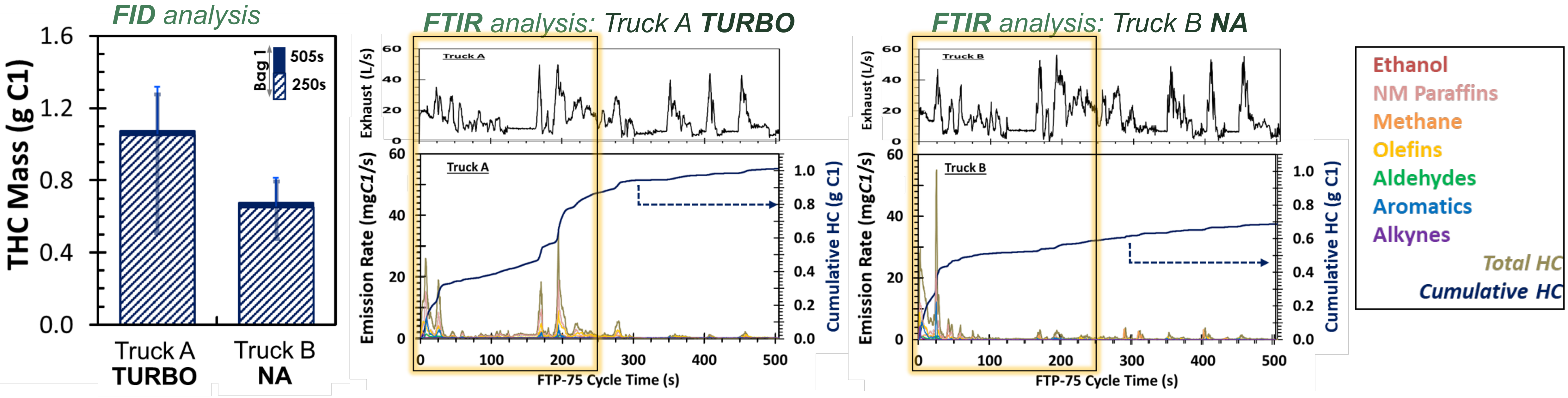




TWC (three-way catalyst);EC/OC (elemental carbon/organic carbon); DNPH (2,4-dinitrophenylhydrazine); LFE (laminar flow element); EEPS (Engine Exhaust Particle Sizer); FTIR (Fourier-transform infrared spectroscopy)

Most Cold-Start (bag 1, 505s) HCs generated in 1st 250s

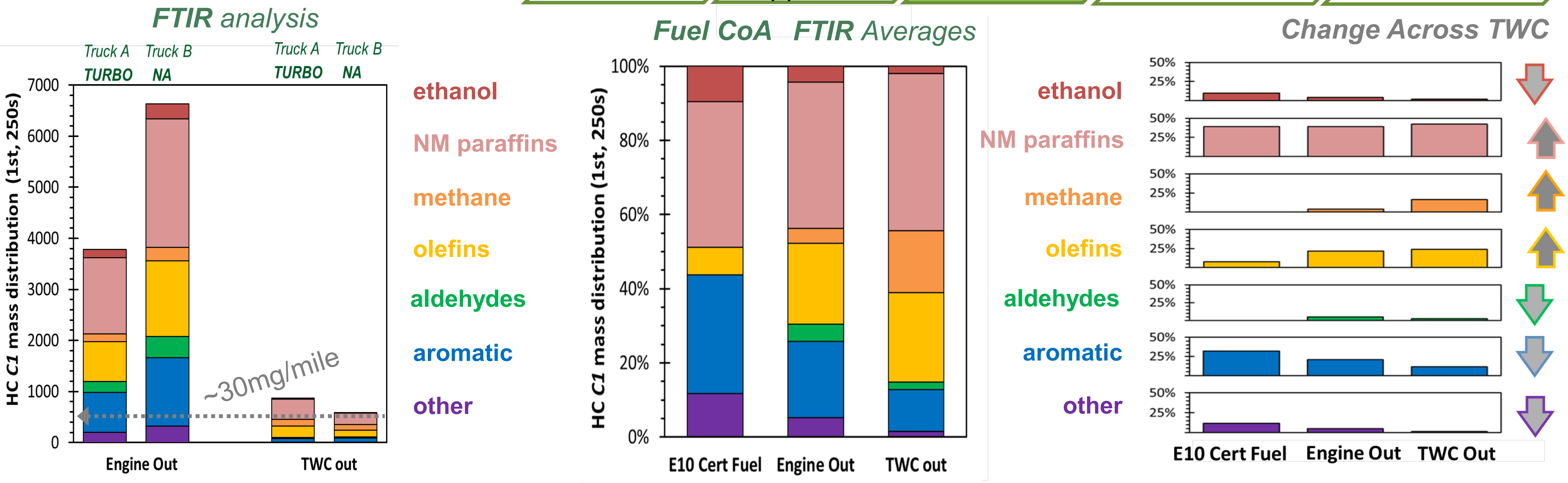
TWC out *Hydrocarbons*



- HC-traps will be located downstream of ccTWC in an underfloor location
- Cold-start HC emission at ccTWC out needed to study HC speciation impact on HC-trap effectiveness
- Greater than 85% of cold-start (bag 1, 505s of FTP-75) HCs in the first 250s
- Effectiveness of HC-traps is not a linear relationship with C1 HC emissions
  - Exhaust HCs more complex than C1 quantity

FID (flame ionization detector); THC (total hydrocarbons); HC (hydrocarbon); NM (non-methane)

Distribution of cold-start HC species change across ccTWC

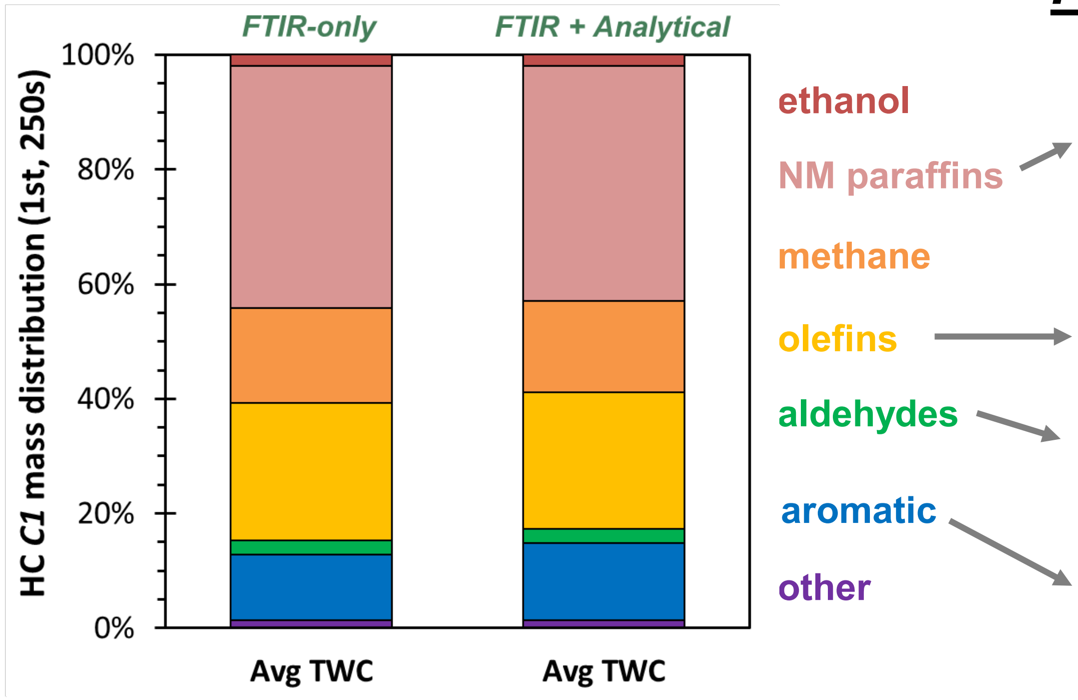


- Significant drop in HC emission across TWC even during Cold-Start
- Both trucks had similar compositional distribution of HC C*1* mass emissions at each location
- Distribution of HC species changes across ccTWC out: not just passing through
- Feed composition for development of ccTWC and HC-trap low temperature activity need to be different
- Cold-start THC at TWC out greater than full FTP targeted Tier 3 Bin 30 target (NMOG + NOx)

CoA (certificate of analysis); cert (certification)

Detailed HC speciation by GC-MS provides identification of HC ≥ C5

TWC out *Hydrocarbons*



FTIR HC Speciation

- *ethane (C2)*
  - *isopentane (C5)*
  - *cyclohexane (C6)*
- *ethylene (C2)*
- *propylene (C3)*
- *1,3 butadiene (C4)*
- *isobutylene (C4)*
- *formaldehyde (C1)*
- *acetaldehyde (C2)*
- *acrolein (C3)*
- *toluene (C7)*

Analytical HC Speciation

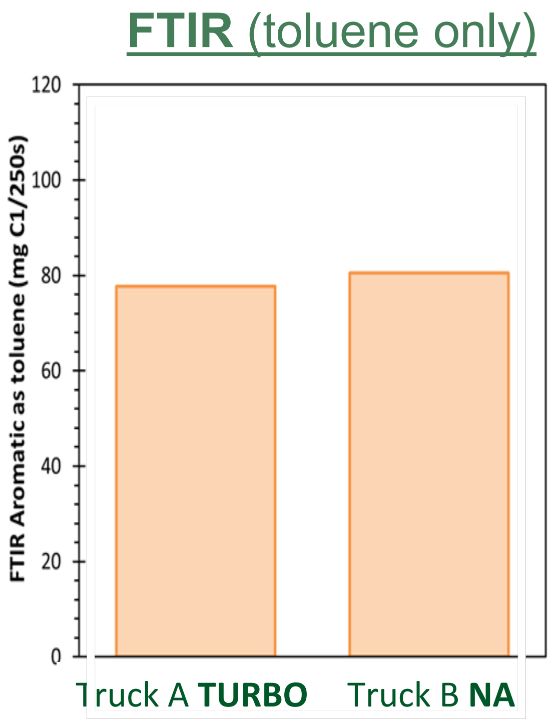
- *pentane (C5)*
- *octane (C8)*
- *13-25 other (≥C5)*
- *1-pentene (C5)*
- *1-hexene (C6)*
- *formaldehyde (C1)*
- *acetaldehyde (C2)*
- *acrolein (C3)*
- *propionaldehyde (C3)*
- *crotonaldehyde (C4)*
- *butylaldehyde (C4)*
- *valeraldehyde (C5)*
- *benzaldehyde (C7)*
- *tolualdehyde (C8)*
- *dimethyl benzaldehyde (C9)*
- *C6-C11 (next slide)*

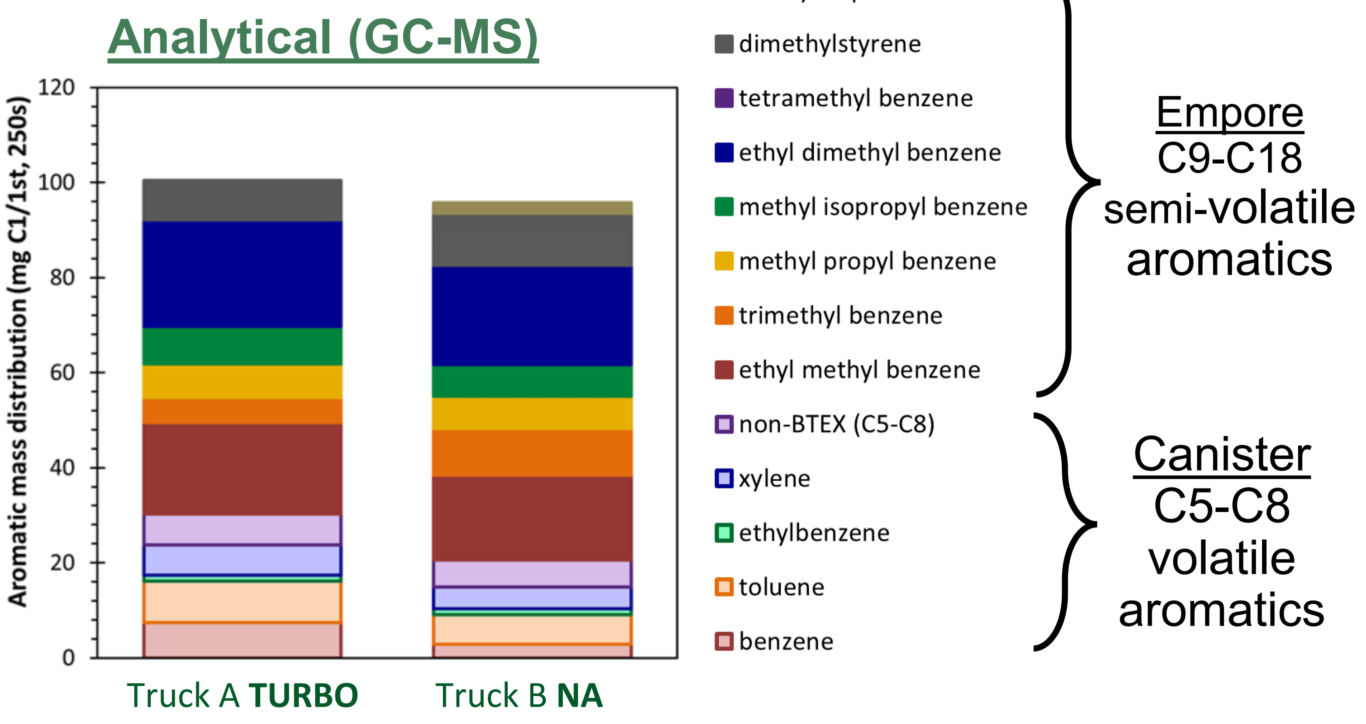
- FTIR is ideal for small chain HC up to ~C4 (Distinct stretching regions)
- Analytical separation and identification by GC-MS provides more detail on species in exhaust
  - Major NM Paraffins: ethane and unbranched pentane and octane only account for ~31% of total TWC out

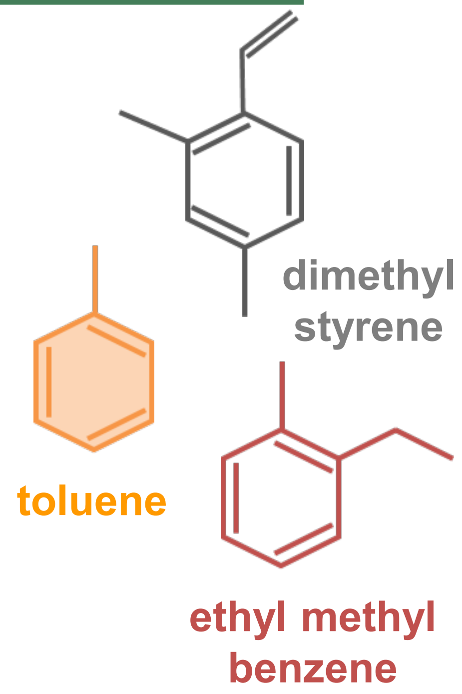
Total regulator C1 Mass (**FID**) → Compositional Distribution (**FTIR major + Analytical minor**)
→ Full HC Speciation (**combination of FTIR + Analytical speciation**)

Cold-start aromatics predominately larger, semi-volatile species

***TWC out** Hydrocarbons*



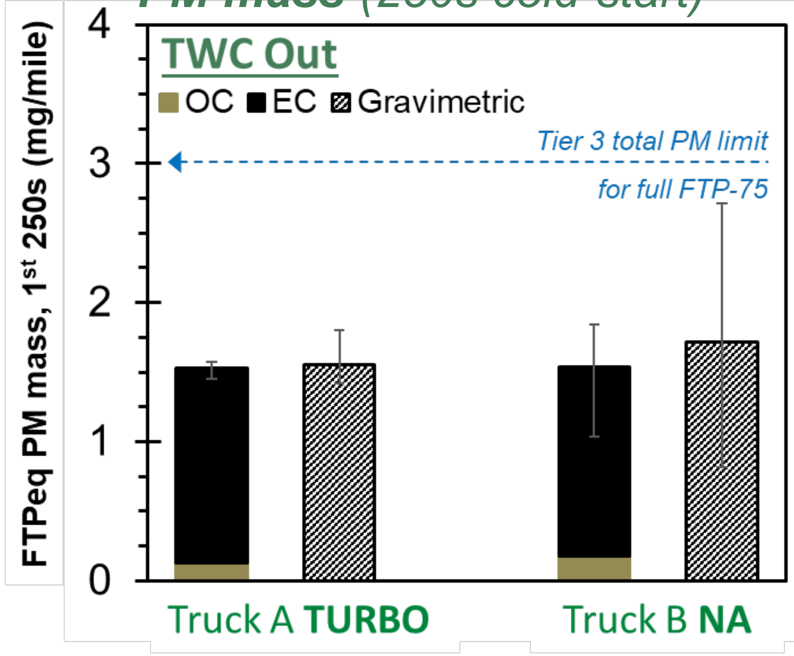




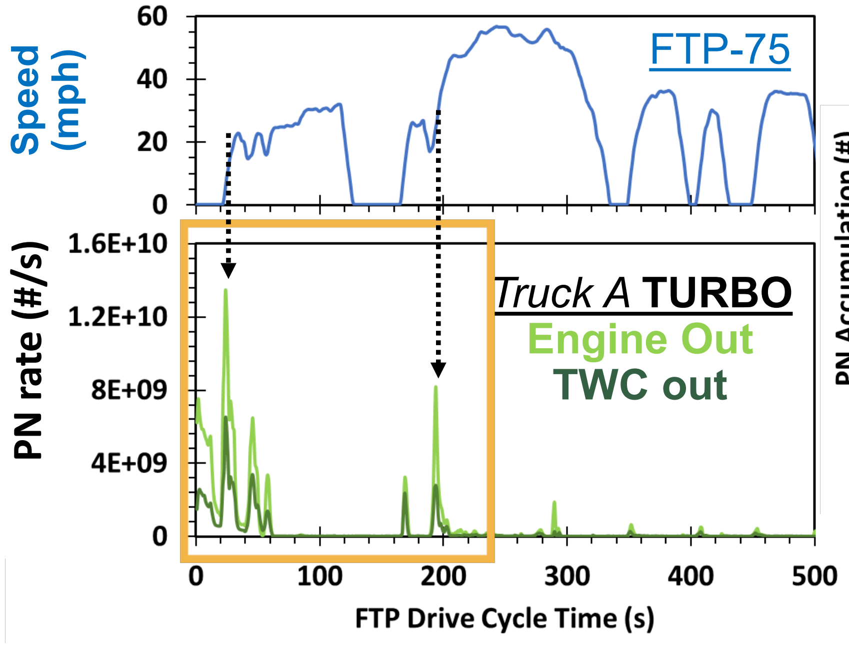
- Aromatics measured by FTIR method are "as C7" or toluene, measure stretch of the aromatic ring
- FTIR aromatic mass accounts for ~80% of total aromatics by analytical speciation (GC-MS)
  - GC-MS only identifies 9% of speciated aromatics as toluene
- TWC out aromatics are mix of fuel species other partial combustion products
- Only one species seen in Engine out speciation not seen at TWC out: tetramethyl benzene

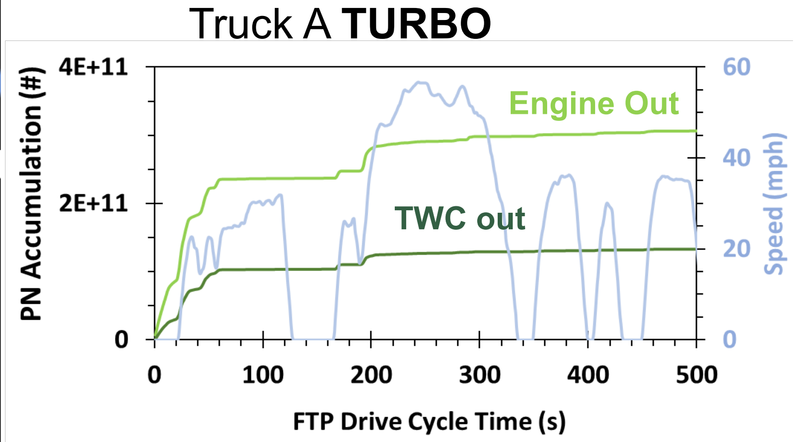
PM mass drop over ccTWC indicated by PN reduction

***PM mass** (250s cold-start)*



Particle Number





- Elemental carbon accounts for ~90% of total PM mass over first 250s
- Equates to nearly half of Tier 3 Bin 30 limit of 3mg total PM over entire FTP drive cycle
- Particle Number correlates to acceleration events in FTP
  - 76- 95% of PN in 1st 250s
- TWC reduces particle PN by 40-44%

PN (particle number)

Response to 2019 Reviewers' Comments

- New Task in FY19;
- No previous reviewer response because 2020 AMR is first review

Collaborations and Coordination

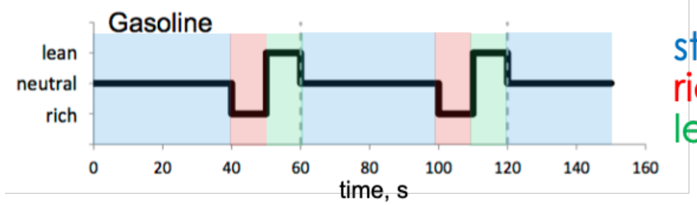
- Collaborations
  - Umicore supplying HC-traps and GPFs for FY20 study
  - Umicore and Ford technical staff acting as informal advisors on technical set-up of HC-trap vehicle testing
    - Umicore: John Nunan and David Moser
    - Ford Motor Co.: Jason Lupescu and Christine Lambert
- Coordination:
  - Share results CLEERS community
- HC-traps aged by SGS
  - according US Drive storage protocol

umicore

Ford

CLEERS Cross-Cut Lean Exhaust Emissions Reduction Simulations

USDRIVE DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY



stoich: 40s, λ=1.0
rich: 10s, λ=0.91
lean: 10s, λ=1.33

stoich/rich/lean cycling for 50 hr at 700 °C inlet temperature

Remaining Challenges and Future Research Plans

Relevance | Approach | Technical | Collaboration | **Future Work**

Remaining Challenges	**Future Work*** *(subject to change with funding levels)*
• Cold-start HC emission need to be reduced to meet future emission standards • HC-traps efficiency can vary by HC species	• Measure detailed HC speciation after under floor HC-trap **(FY20)** • Study impact HC-trap + GPF on HC speciation during cold-start **(FY20)**
• Hybridization may reduce catalyst activity beyond vehicle cold-start due to drop in exhaust temperatures when engine is off	• Evaluate the impact of hybridized vehicle on HC emissions **(FY21)** • Measure the HC-trap trapping efficiency and speciation effectiveness from hybridized vehicle **(FY21)**

Summary

- Relevance
  - Hydrocarbon reduction during cold-starts when oxidation catalysts are not active will be needed to meet the more stringent HC emission standards for Tier 3 Bin 30 and beyond. HC-traps offer a potential solution but do not work uniformly for all hydrocarbon species.
- Approach
  - Use a chassis dynamometer to collect cold-start exhaust samples over the first 250s of FTP-75 drive cycle from consumer light-duty GDI pick-ups and collect analytical samples for detailed HC speciation by GC-MS
  - Evaluate which specific HC species are effectively trapped on a supplier developed HC-trap during cold-start
- Technical Accomplishments
  - Detailed speciation of HCs during first 250s of FTP cold-start at engine out and close-coupled TWC out. TWC out will be used as HC-trap In during FY20 study of HC-traps.
- Collaborations
  - Umicore and Ford technical experts are providing guidance on proper HC-trap testing on vehicles
  - Umicore supplying HC-traps and catalyzed GPFs
- Future Work
  - Vehicle evaluation of HC-trap and a HC-trap + GPF impact on the detail HC speciation of the cold-start emissions
  - Investigate the use of HC-traps for control of hydrocarbon emissions from hybridized vehicles.

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TECHNICAL BACK UP SLIDES

How to study the chemistry of cold-start emissions

Relevance | **Approach** | Technical | Collaboration | Future Work

Vehicle Platforms on Chassis Dynamometer

Truck A and Truck B: MY18, GDI pick-up trucks (25-30k on-road miles)

	Engine	Exhaust Modifications
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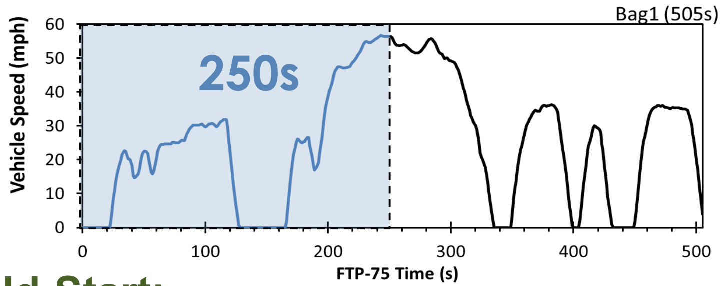

Cold-Start:

- 1 cold-start/truck per day (cold-start = 12hr soak)
- 1st, 250s of FTP-751

Sampling:

P	Time	Engine Out	TWC Out	HC-trap Out	HC-trap +GPF Out	Speciation/Analyzed	Method
Bag	**250s/505s**	✓	✓	*FY20*	*FY20*	Total HC, NOx, CO, CO2 (ppm)	FID, (CAI emissions analyzers)
Canister	**250s**	✓	✓	*FY20*	*FY20*	C_5-C_8 Hydrocarbons (ng/L)	GC-MS
Empore	**250s**	✓	✓	*FY20*	*FY20*	C_9-C_{18} Hydrocarbons (ng/L)	Extraction + GC-MS
DNPH	**250s**	✓	✓	*FY20*	*FY20*	Aldehydes (ng/L)	Extraction + HPLC-MS or HPLC-UV-Vis
PM mass	**250s**		✓	*FY20*	*FY20*	Particulate Matter (mg/L)	Gravimetric
PM EC/OC	**250s**		✓	*FY20*	*FY20*	Elemental & Organic Carbon (mg/L)	Thermal-Optical
EEPS	**250s/505s**	✓	✓	*FY20*	*FY20*	PN (#/s) and Size Distribution (nm) *time resolved (10Hz)*	Array of Electrometers (electrical mobility)
FTIR	**250s/505s**	✓	✓	*FY20*	*FY20*	Gaseous Concentrations (ppm) *time resolved (5Hz)*	IR (stretching frequency)

ABBREVIATIONS for Slide 6

CUC	Clean-up catalyst
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
GOC	Gasoline oxidation catalyst
GPF	Gasoline particulate filter
HCT	Hydrocarbon trap
LNT	Lean NOx trap
PNA	Passive NOx adsorber
SCR	Selective catalytic reduction
TWC	Three-way catalyst

Stoich	Stoichiometric
SI	Spark ignited
CDC	Conventional diesel combustion
LTC	Low temperature combustion
ACI	Advanced compression ignition
PNA	Passive NOx adsorber
rpm	Revolutions per minute
BMEP	Brake mean effective pressure